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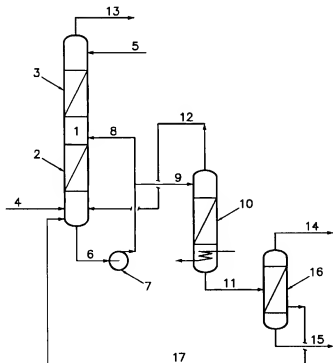
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(54) Title: PROCESS FOR PURIFYING HYDROGEN CHLORIDE

Fig. 1

(57) Abstract: Process for purifying hydrogen chloride,  
comprising at least one step of bringing said hydrogen  
chloride into contact with a scrubbing agent containing  
at least one chlorohydrin.



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Process for purifying hydrogen chloride

The present patent application claims the benefit of the following patent application FR 0856138 filed on 12 September 2008, the content of which is incorporated here by reference.

The present invention relates to a process for purifying hydrogen chloride (HCl). It relates more particularly to a process for purifying hydrogen chloride gas that contains aromatic organic compounds, in particular chlorinated aromatic compounds. It also relates to a process for manufacturing a chlorohydrin by hydrochlorination of a polyhydroxylated aliphatic hydrocarbon, using the hydrogen chloride obtained via the purification process according to the invention. It also relates to a process for manufacturing an epoxide by dehydrochlorination of the chlorohydrin obtained, and also to processes for manufacturing products derived from the epoxide.

A large number of industrial chemical processes generate hydrogen chloride, especially hydrogen chloride gas, as a by-product. Mention may be made, from among the most commonly practised, of the production of vinyl chloride, the production of chloromethanes and chlorinated solvents, the molecule of which contains at least two carbon atoms, the synthesis of isocyanates and the synthesis of fluorinated hydrocarbons.

This production of large quantities of hydrogen chloride raises the problem of its purification when it must be re-used as a raw material for other processes.

When the hydrogen chloride originates from processes for the manufacture of diisocyanates, toluene diisocyanate, 4,4'-diphenylmethane diisocyanate or hexamethylene-1,6-diisocyanate for example, this hydrogen chloride is contaminated with aromatic organic compounds, such as monochlorobenzene and dichlorobenzenes.

Thus, concerning the production of epichlorohydrin, it has been found that the synthesis process via alkaline dehydrochlorination of dichloropropanol obtained by hydrochlorination of glycerol necessitates using, in the hydrochlorination step, a hydrogen chloride that has previously been purified if it is desired to prevent contaminants of the hydrogen chloride from occurring in the epichlorohydrin and the products derived from the latter.

The processes for purifying hydrogen chloride proposed in the prior art have some disadvantages.

Solvent scrubbing processes, such as that mentioned in French patent 1417388, have the drawback that the compound used for the scrubbing in turn contaminates the hydrogen chloride and that the disposal of this compound raises a problem associated with the fact that the hydrogen chloride is still at least partially soluble in the liquid phase of said compound.

Another process for purifying hydrogen chloride, which can be used as a reactant in an ethylene oxychlorination step, by scrubbing with 1,2-dichloroethane is mentioned in document FR 2 881 732.

The processes that make use of fractional distillation including a condensation step, of adsorption or absorption by suitable liquids or solids, and of catalytic hydrogenation or oxidation reactions, as mentioned in document EP-B-0 774 450, have drawbacks associated sometimes with the complexity of the apparatus to be used, sometimes with the need to regenerate the adsorbents or absorbents used, loaded in turn with the impurities present in the hydrogen chloride to be purified, or else with the need to regenerate the costly hydrogenation or oxidation catalysts used.

Processes which consist in converting hydrogen chloride gas to hydrochloric acid and in then bringing this hydrochloric acid into contact with an anion exchange resin, as described in document EP-A-0 618 170, constitute complicated and costly solutions.

Purification processes that rest on a two-stage condensation with recycling of the coldest condensed phase from the second stage to the first, as described in document US-A-2004/016411, make use of complex devices comprising a costly refrigeration unit requiring high energy consumption. Furthermore, the efficiency of this type of purification is limited by the vapour pressure of the compounds to be removed, at the temperature reached at condensation.

The present invention aims to provide a process for purifying hydrogen chloride that does not have these drawbacks.

The present invention hence relates in a first aspect to a process for purifying hydrogen chloride, comprising at least one step of bringing said hydrogen chloride into contact with a scrubbing agent containing at least one chlorohydrin.

The hydrogen chloride may be in the form of a liquid, a gas, an aqueous solution or a combination of at least two of these forms. The hydrogen chloride is often in the gaseous state.

The hydrogen chloride may contain various types of impurities. These  
5 impurities may be organic compounds, inorganic compounds, or mixtures of them. The hydrogen chloride often contains organic compounds, and frequently aromatic organic compounds.

The impurity content of the hydrogen chloride is generally greater than or equal to 100 ppm by weight, usually greater than or equal to 1000 ppm by  
10 weight and often greater than or equal to 10 000 ppm by weight. This content is usually less than or equal to 10 % by weight, frequently less than or equal to 5 % by weight and in a lot of cases less than or equal to 2 % by weight.

The process according to the invention preferably applies to the purification of hydrogen chloride resulting from syntheses involving the  
15 presence of aromatic organic compounds. On account of this origin, this hydrogen chloride contains, as impurities, one or more aromatic organic compounds, the standard boiling point of which is generally above 100°C, compounds that are at least partially soluble in the scrubbing agent or miscible therewith. Preferably, the hydrogen chloride to be purified is the by-product of  
20 the manufacture of organic isocyanates. More preferably, the hydrogen chloride to be purified is the by-product of the manufacture of organic isocyanates by reacting phosgene with an organic amine, usually an aromatic amine and preferably an aromatic diamine. In this particular case, the impurities are most frequently chloroaromatic compounds, typically monochlorobenzene and  
25 dichlorobenzene, used as solvents in this manufacture. The dichlorobenzene may be chosen from 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and mixture of at least two of these isomers.

The chloroaromatic impurity content of the hydrogen chloride is generally greater than or equal to 100 ppm by weight, usually greater than or equal  
30 to 1000 ppm by weight and often greater than or equal to 10 000 ppm by weight. This content is usually less than or equal to 10 % by weight, frequently less than or equal to 5 % by weight and in a lot of cases less than or equal to 2 % by weight.

In the present description, the expression "scrubbing agent containing at  
35 least one chlorohydrin" or more simply "scrubbing agent" is understood to mean

a composition in which at least one portion of the chlorohydrin is present in the liquid state.

The scrubbing agent that can be used according to the present invention often contains at least one chlorohydrin mainly in the liquid state.

5 The expression "chlorohydrin" is used here to describe a compound containing at least one hydroxyl group and at least one chlorine atom attached to various saturated carbon atoms. The chlorohydrins may be chosen from chloroethanol, chloropropanol, chloropropanediol, dichloropropanol and mixtures of at least two of them. The chlorohydrins are generally chosen from  
10 monochloropropanediol, dichloropropanol, and mixtures thereof. Monochloropropanediol is often used. Dichloropropanol is very suitable. The chlorohydrins that are more particularly encountered are chosen from 2-chloroethanol, 1-chloropropane-2-ol, 2-chloropropane-1-ol, 1-chloropropane-3-ol, 1-chloropropane-2,3-diol, 2-chloropropane-1,3-diol,  
15 1,3-dichloropropane-2-ol, 2,3-dichloropropane-1-ol, chlorohydrins of polyglycerol such as the diglycerol of linear or cyclic structure, and mixtures of at least two of them. The chlorohydrins that are often encountered are diglycerol monochlorohydrin, diglycerol dichlorohydrin, diglycerol trichlorohydrin, 1-chloropropane-2,3-diol, 2-chloropropane-1,3-diol, and mixtures of at least two  
20 of them. Chlorohydrins that are frequently encountered are 1,3-dichloropropane-2-ol, 2,3-dichloropropane-1-ol, and mixtures thereof.

The presence, in said scrubbing agent, of other compounds capable of solubilizing the impurity (impurities) present in the hydrogen chloride to be purified or of forming a liquid mixture with it (them) is not at all excluded from  
25 the context of the invention.

The content of chlorohydrin in the scrubbing agent is generally greater than or equal to 100 g of chlorohydrin per kg of scrubbing agent, usually greater than or equal to 200 g/kg, habitually greater than or equal to 300 g/kg, in a lot of cases greater than or equal to 400 g/kg and often greater than or equal to 500 g/kg.  
30 This content is generally less than or equal to 950 g/kg, often less than or equal to 900 g/kg, frequently less than or equal to 800 g/kg and in a lot of cases less than or equal to 700 g/kg.

The content of chlorohydrin in the scrubbing agent may also be greater than or equal to 950 g/kg, sometimes greater than or equal to 990 g/kg and in  
35 certain cases greater than or equal to 999 g/kg. A scrubbing agent composed

mainly of at least one chlorohydrin is very suitable. A scrubbing agent composed mainly of dichloropropanol is very particularly suitable.

Most particularly, the scrubbing agent is substantially composed of chlorohydrin in the liquid state, more specifically in the case where the hydrogen chloride to be purified is intended to be used in a process for the hydrochlorination of a polyhydroxylated aliphatic hydrocarbon, intended to produce a chlorohydrin. In this case, an essential advantage of the process of the invention lies in the fact that the presence of this chlorohydrin is in no way troublesome, since it is a compound formed during this hydrochlorination.

The scrubbing agent according to the invention may additionally contain at least one compound chosen from water, alcohols, aldehydes, ketones, carboxylic acids, carboxylic acid esters, ethers, halogenated hydrocarbons, epoxides, metals, in the metallic state or in the salt state, and mixtures of at least two of them. The chlorohydrins are not considered to be alcohols or halogenated hydrocarbons or ethers or esters. This case is encountered often when the scrubbing agent originates from the purge of a process for the manufacture of a chlorohydrin by hydrochlorination of a polyhydroxylated aliphatic hydrocarbon.

The content of water in the scrubbing agent is generally greater than or equal to 0.01 g/kg, usually greater than or equal to 0.1 g/kg, commonly greater than or equal to 1 g/kg, often greater than or equal to 5 g/kg, frequently greater than or equal to 10 g/kg, and particularly greater than or equal to 20 g/kg. This water content is generally less than or equal to 300 g/kg, usually less than or equal to 200 g/kg, commonly less than or equal to 150 g/kg, often less than or equal to 100 g/kg, frequently less than or equal to 70 g/kg and particularly less than or equal to 50 g/kg.

The alcohols may be chosen from monoalcohols, diols, polyols other than diols, and mixtures of at least two of them.

The monoalcohols may be chosen from 2-propanol, allyl alcohol, chloroethanols, often 2-chloroethanol, chloropropanols, often 3-chloro-1-propanol, chloropropenols, often 2-chloropropenol, phenol, and mixtures of at least two of them.

The content of monoalcohol in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.005 g/kg, commonly greater than or equal to 0.01 g/kg, often greater than or equal to 0.02 g/kg, frequently greater than or equal to 0.04 g/kg, and particularly greater than or equal to 0.05 g/kg. This monoalcohol content is generally less

than or equal to 20 g/kg, usually less than or equal to 10 g/kg, commonly less than or equal to 5 g/kg, often less than or equal to 2 g/kg, frequently less than or equal to 1 g/kg and particularly less than or equal to 0.1 g/kg.

- 5 The diols may be chosen from 1,3-propanediol, 1,2-propanediol, butanediol, and mixtures of at least two of them.

The content of diol in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.005 g/kg and frequently greater than or equal to 0.01 g/kg. This diol content is generally less than or equal to 40 g/kg, usually less than or equal to 20 g/kg, commonly less than or equal to 10 g/kg, often less than or equal to 5 g/kg, frequently less than or equal to 1 g/kg and particularly less than or equal to 0.5 g/kg.

An example of a polyol other than a diol is glycerol.

The content of polyol other than a diol in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.01 g/kg, commonly greater than or equal to 0.1 g/kg, often greater than or equal to 1 g/kg, frequently greater than or equal to 2 g/kg, and particularly greater than or equal to 5 g/kg. This content of polyol other than a diol is generally less than or equal to 100 g/kg, usually less than or equal to 80 g/kg, commonly less than or equal to 60 g/kg, often less than or equal to 50 g/kg, frequently less than or equal to 20 g/kg and particularly less than or equal to 10 g/kg.

- 20 The aldehydes may be chosen from acetaldehyde, acrolein, and mixtures thereof.

The content of aldehyde in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.005 g/kg, commonly greater than or equal to 0.01 g/kg, often greater than or equal to 0.015 g/kg, frequently greater than or equal to 0.02 g/kg, and particularly greater than or equal to 0.05 g/kg. This aldehyde content is generally less than or equal to 10 g/kg, usually less than or equal to 5 g/kg, commonly less than or equal to 2 g/kg, often less than or equal to 1 g/kg, frequently less than or equal to 0.5 g/kg and particularly less than or equal to 0.1 g/kg.

- 30 The ketones may be chosen from acetone, butanones, often 2-butanone, hydroxyacetone, chloroacetone, pentanediones, often 2,3-pentanedione, cyclopentanone, methylcyclopentenones, often 2-methyl-2-cyclopentene-1-one, and mixtures of at least two of them.

35 The content of ketone in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.005 g/kg, commonly



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greater than or equal to 0.01 g/kg, often greater than or equal to 0.05 g/kg, frequently greater than or equal to 0.1 g/kg, and particularly greater than or equal to 0.5 g/kg. This ketone content is generally less than or equal to 10 g/kg, usually less than or equal to 8 g/kg, commonly less than or equal to 6 g/kg, often less than or equal to 4 g/kg, frequently less than or equal to 2 g/kg and particularly less than or equal to 1 g/kg.

The carboxylic acids may be chosen from monocarboxylic acids, polycarboxylic acids, often dicarboxylic acids, and mixtures of at least two of them. Acetic acid is an example of a monocarboxylic acid. Adipic acid is an example of a dicarboxylic acid.

The content of carboxylic acid in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.01 g/kg, commonly greater than or equal to 0.1 g/kg, often greater than or equal to 0.5 g/kg, frequently greater than or equal to 1 g/kg, and particularly greater than or equal to 5 g/kg. This carboxylic acid content is generally less than or equal to 100 g/kg, usually less than or equal to 80 g/kg, commonly less than or equal to 60 g/kg, often less than or equal to 40 g/kg, frequently less than or equal to 20 g/kg and particularly less than or equal to 10 g/kg.

The carboxylic acid esters may be chosen from the esters of the aforementioned acids with chlorohydrins and alcohols. In particular, these esters may be chosen from the adipates of glycerol, of diglyccrol, of monochloropropanediol, of dichloropropanol, and mixtures of at least two of them.

The content of carboxylic acid ester in the scrubbing agent is generally greater than or equal to 0.01 g/kg, usually greater than or equal to 0.1 g/kg, commonly greater than or equal to 1 g/kg, often greater than or equal to 5 g/kg, frequently greater than or equal to 10 g/kg, and particularly greater than or equal to 15 g/kg. This carboxylic acid ester content is generally less than or equal to 500 g/kg, usually less than or equal to 300 g/kg, commonly less than or equal to 150 g/kg, often less than or equal to 100 g/kg, frequently less than or equal to 50 g/kg and particularly less than or equal to 20 g/kg.

The halogenated hydrocarbons may be chosen from monochloropropanes, often 2-chloropropane, monochloropropenes, often allyl chloride, dichloropropanes, often 1,3-dichloropropane, dichloropropenes, often *cis*-1,3-dichloropropene, frequently *trans*-1,3-dichloropropene, trichloropropanes,

often 1,2,3-trichloropropane, chlorobromopropanes, and mixtures of at least two of them.

The content of halogenated hydrocarbons in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.005 g/kg, commonly greater than or equal to 0.01 g/kg, often greater than or equal to 0.05 g/kg, frequently greater than or equal to 0.1 g/kg, and particularly greater than or equal to 0.5 g/kg. This halogenated hydrocarbon content is generally less than or equal to 20 g/kg, usually less than or equal to 10 g/kg, commonly less than or equal to 5 g/kg, often less than or equal to 3 g/kg, frequently less than or equal to 2 g/kg and particularly less than or equal to 1 g/kg.

Epichlorohydrin is an example of an epoxide.

The content of epoxide in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.005 g/kg, commonly greater than or equal to 0.01 g/kg, often greater than or equal to 0.05 g/kg, frequently greater than or equal to 0.1 g/kg, and particularly greater than or equal to 0.5 g/kg. This epoxide content is generally less than or equal to 10 g/kg, usually less than or equal to 8 g/kg, commonly less than or equal to 6 g/kg, often less than or equal to 4 g/kg, frequently less than or equal to 2 g/kg and particularly less than or equal to 1 g/kg.

The ethers may be chosen from polyglycerols, often diglycerols, frequently diglycerols of linear structure or of cyclic structure, and mixtures thereof.

The content of ethers in the scrubbing agent is generally greater than or equal to 0.005 g/kg, usually greater than or equal to 0.01 g/kg, commonly greater than or equal to 0.05 g/kg, often greater than or equal to 0.1 g/kg, frequently greater than or equal to 0.5 g/kg, and particularly greater than or equal to 1 g/kg. This ether content is generally less than or equal to 50 g/kg, usually less than or equal to 40 g/kg, commonly less than or equal to 30 g/kg, often less than or equal to 20 g/kg, frequently less than or equal to 10 g/kg and particularly less than or equal to 5 g/kg.

The metals in the metallic state or in the salt state may be chosen from iron, nickel, chromium, calcium, sodium, and mixtures of at least two of them.

The content of metals in the metallic state or in the salt state, expressed as elemental metal, in the scrubbing agent is generally greater than or equal to 0.001 g/kg, usually greater than or equal to 0.005 g/kg, commonly greater than or equal to 0.01 g/kg, often greater than or equal to 0.05 g/kg, frequently greater

than or equal to 0.1 g/kg, and particularly greater than or equal to 0.5 g/kg. This metal content is generally less than or equal to 20 g/kg, usually less than or equal to 15 g/kg, commonly less than or equal to 10 g/kg, often less than or equal to 5 g/kg, frequently less than or equal to 2 g/kg and particularly less than or equal to 1 g/kg.

The metals may be present in the form of metal salts. These salts may be organic or inorganic salts. The expression "inorganic salts" is understood to mean salts for which the constituent ions do not contain a carbon-carbon bond or a carbon-hydrogen bond. The expression "organic salts" is understood to mean salts for which at least one of the constituent ions contains at least one carbon-carbon bond or one carbon-hydrogen bond. The metal salts may be chosen from metal chlorides, sulphates, hydrogensulphates, hydroxides, carbonates, hydrogencarbonates, phosphates, hydrogenphosphates, nitrates or borates, and mixtures of at least two of them.

The various impurities may advantageously be present in the hydrogen chloride in the form of droplets, solid particles or gaseous fractions.

The process according to the invention is advantageously carried out at any pressure compatible with keeping at least one portion of the hydrogen chloride to be purified in the gaseous state, often compatible with keeping the hydrogen chloride to be purified entirely in the gaseous state. This pressure is generally greater than or equal to 1 bar and often greater than or equal to 5 bar. This pressure is usually less than or equal to 20 bar and frequently less than or equal to 15 bar. A pressure in the vicinity of 10 bar is very suitable.

The temperature at which the process is carried out may be easily chosen by a person skilled in the art in order to promote the dissolution and/or absorption of the impurities in the scrubbing agent and taking account of the vapour pressure values of the aromatic organic compounds present as impurities in the hydrogen chloride to be purified. This temperature is generally greater than or equal to 10°C, often greater than or equal to 20°C, frequently greater than or equal to 50°C and in a lot of cases greater than 75°C. This temperature is customarily less than or equal to 120°C, often less than or equal to 100°C and sometimes less than 90°C. Values close to ambient temperature (about 25°C) are very suitable, for example in the case where the scrubbing agent is mainly composed of chlorohydrin, such as dichloropropanol. Values close to 80°C are very suitable, for example when the scrubbing agent originates from the purge of

a process for the manufacture of a chlorohydrin by hydrochlorination of a polyhydroxylated aliphatic hydrocarbon.

The ratio between the respective flows of scrubbing agent and hydrogen chloride to be purified is not critical and can vary to a large extent. It is in practice limited only by the cost of the possible regeneration of the scrubbing agent. The flow of scrubbing agent, expressed as a weight percentage relative to the flow of hydrogen chloride to be purified, is generally greater than or equal to 0.5, often greater than or equal to 1 and frequently greater than or equal to 2. This flow is usually less than or equal to 50, frequently less than or equal to 20 and often less than or equal to 10.

The ratio between the respective quantities of scrubbing agent and hydrogen chloride to be purified is not critical and can vary to a large extent. It is in practice limited only by the cost of the possible regeneration of the scrubbing agent. The quantity of scrubbing agent, expressed as a weight percentage relative to the quantity of hydrogen chloride to be purified, is generally greater than or equal to 0.5, often greater than or equal to 1, frequently greater than or equal to 2, and in particular greater than or equal to 10. This quantity is usually less than or equal to 80, frequently less than or equal to 60, often less than or equal to 40 and in particular less than or equal to 20.

The contacting step of the process according to the invention may be carried out in continuous mode, semi-continuous mode or batch mode. The expression "continuous mode" is understood to denote an operating mode which is continuous for the gas phase and continuous for the liquid phase. The expression "semi-continuous mode" is understood to denote an operating mode which is continuous for the gas phase and in batch mode for the liquid phase. The expression "batch mode" is understood to denote an operating mode which is in batch mode for the gas phase and in batch mode for the liquid phase. It is preferred to operate in semi-continuous or continuous mode. Continuous mode is preferred.

When the process is carried out in batch mode, the duration of the contacting step between the scrubbing agent and the hydrogen chloride to be purified is generally greater than or equal to 0.01 min, often greater than or equal to 0.02 min and frequently greater than or equal to 0.05 min. This duration is usually less than or equal to 60 min, commonly less than or equal to 40 min, and frequently less than or equal to 20 min.

When the process is carried out in continuous mode, the residence time of the gas phase during the contacting step between the scrubbing agent and the hydrogen chloride to be purified is generally greater than or equal to 1 s, often greater than or equal to 2 s and frequently greater than or equal to 3 s. This residence time is usually less than or equal to 120 s, commonly less than or equal to 90 s, and frequently less than or equal to 60 s.

When the process is carried out in continuous mode, the residence time of the liquid phase during the contacting step between the scrubbing agent and the hydrogen chloride to be purified is generally greater than or equal to 10 s, often greater than or equal to 15 s and frequently greater than or equal to 20 s. This residence time is usually less than or equal to 60 min, commonly less than or equal to 50 min, and frequently less than or equal to 45 min.

When the process is carried out in semi-continuous mode, the residence time of the gas phase during the contacting step between the scrubbing agent and the hydrogen chloride to be purified is generally greater than or equal to 1 s, often greater than or equal to 2 s and frequently greater than or equal to 3 s. This residence time is usually less than or equal to 120 s, commonly less than or equal to 90 s, and frequently less than or equal to 60 s.

The proportion of impurities present in the hydrogen chloride to be purified before the step of contacting with the scrubbing agent, and which is found in the scrubbing agent at the end of this step, is generally greater than or equal to 50 %, in many cases greater than or equal than 60 %, commonly greater than or equal than 70 %, often greater than or equal than 80 %, usually greater than or equal to 90 %, frequently greater than or equal to 99 %, more often greater than or equal to 99.99 % and in a lot of cases greater than or equal to 99.999 %.

The process according to the invention comprises at least one step of bringing the hydrogen chloride into contact with the scrubbing agent. Preferably, and in the case of operating moreover in continuous mode, the process is however carried out in two steps ; one of the steps thus comprises loop flow (recycling) of the scrubbing agent and the other step comprises a supply of fresh scrubbing agent. In this case, the flow of fresh scrubbing agent, expressed as a weight percentage of the flow of hydrogen chloride to be purified, is generally greater than or equal to 0.1, often greater than or equal to 1 and frequently greater than or equal to 3. This flow is commonly less than or equal

to 20, often less than or equal to 10, and in a lot of cases less than or equal to 7. Such a flow in the vicinity of 5 percent by weight is very suitable.

The liquid mixture or the solution (referred to as fraction (f) below) comprising the scrubbing agent, loaded with the impurities extracted from the hydrogen chloride to be purified, and also the portion of this hydrogen chloride that is dissolved in or mixed with the said scrubbing agent, may then be treated, at least partly, by any known means, especially to separate the hydrogen chloride therefrom, and/or the impurities extracted, for example, by scrubbing, by neutralization, by settling, by filtration of the "dead end filtration" type, of the "cross filtration" type, or by means of membranes, such as ceramic membranes for example, by distillation, by absorption, by stripping, etc. The treatment may be carried out by one or by a combination of at least two of these means. The particular implementation of one of these means may be carried out in one or more devices ; in particular when it is a stripping, settling or filtration treatment. In the case of a stripping treatment, the treatment may be carried out in one or more stripping columns, often in several columns and frequently in two columns.

It is preferable to separate the hydrogen chloride from the scrubbing agent loaded with impurities by subjecting all or at least part of the fraction (f) to a stripping operation. Preferably, only part of the fraction (f) is subjected to a stripping operation. For this purpose, the fraction (f) is advantageously divided into a liquid fraction (f1) and a liquid fraction (f2). This division may be carried out using any device known for separating a liquid stream into two and for regulating the resulting flows, such as a tee fitting equipped with flow control valves, for example. In the case where the purification process according to the invention is carried out in continuous mode, the fraction (f1) is then advantageously recycled to the step of contacting the hydrogen chloride with the scrubbing agent. The fraction (f2) (also referred to as the "purge stream") is itself advantageously subjected to the stripping operation mentioned above, during which operation, on the one hand, the hydrogen chloride contained in this fraction (f2) - which may be recycled to the step of contacting with the scrubbing agent - and, on the other hand, the remainder of the purge stream essentially comprising the residue of the scrubbing agent loaded with impurities and referred to below as the residual purge stream, are separated.

In a first embodiment where the scrubbing agent is substantially composed of chlorohydrin in the liquid state, this residual purge stream may advantageously be reused by conveying it to a unit in which the chlorohydrin, the

contaminants with boiling points below that of the chlorohydrin and the contaminants with boiling points above that of the chlorohydrin are separated by distillation. The chlorohydrin obtained may be used for any purpose, preferably it is subjected to a dehydrochlorination reaction in order to produce an epoxide.

5 In a second embodiment where the scrubbing agent is substantially composed of a purge stream from a process for the hydrochlorination of a polyhydroxylated hydrocarbon, in the liquid state, this residual purge stream may advantageously be reused by conveying it to a unit in which a high-temperature oxidation is carried out. The hydrocarbon-based content of the purge stream is  
10 reused in the form of energy and the chlorocarbon-based content of the purge stream is converted to hydrogen chloride. This hydrogen chloride may be reused in the form of an aqueous solution of hydrogen chloride or returned to the step of contacting with the scrubbing agent.

In a third embodiment where the scrubbing agent is substantially composed  
15 of a purge stream from a process for the hydrochlorination of a polyhydroxylated hydrocarbon, in the liquid state, the purge stream (f2) may advantageously be reused by conveying it to a unit in which a high-temperature oxidation is carried out. The hydrocarbon-based content of the purge stream is reused in the form of energy and the chlorocarbon-based content of the purge stream is converted to  
20 hydrogen chloride. This hydrogen chloride may be reused in the form of an aqueous solution of hydrogen chloride or returned to the step of contacting with the scrubbing agent. In this case, the purge stream (f2) is not first subjected to the stripping operation.

The respective proportions of the mass flow of the fraction (f2) to the mass  
25 flow of supply of fresh scrubbing agent is generally greater than or equal to 50 %, often greater than or equal to 60 % and frequently greater than or equal to 70 %. This ratio is generally less than or equal to 500 %, often less than or equal to 200 %, frequently less than or equal to 160 % and in a lot of cases less than or equal to 140 %.

30 The purification process according to the invention is highly efficient.

The proportion of aromatic organic impurities present in the hydrogen chloride to be purified before the step of contacting with the scrubbing agent, and which is found in the scrubbing agent at the end of this step is generally greater than or equal to 50 %, in many cases greater than or equal to 60 %, commonly  
35 greater than or equal to 70 %, often greater than or equal to 80 %, usually greater

than or equal to 90 %, frequently greater than or equal to 99 %, often greater than or equal to 99.99 % and in a lot of cases greater than or equal to 99.999 %.

This process makes it possible to reduce the level of aromatic organic impurities in the purified hydrogen chloride, commonly to less than 500 ppm  
5 generally to less than 100 ppm by weight, usually to less than 50 ppm, in many cases to less than 25 ppm, often to less than 10 ppm, frequently to less than 5 ppm and specifically to less than 1 ppm and particularly to less than 0.5 ppm. This level is generally greater than or equal to 1 ppb. In the case of the chloroaromatic compounds mentioned above, it is possible to attain, by virtue of  
10 the process according to the invention, a residual content in the purified hydrogen chloride that does not exceed 10 ppm.

The process according to the invention has the advantage of making it possible to prevent the contamination, by impurities present in the hydrogen chloride, of products resulting from a manufacture that uses hydrogen chloride.

15 The step of bringing the hydrogen chloride into contact with the scrubbing agent may be carried out in any type of device, in particular the devices intended for the contacting of gases and liquids. Devices of this type are described in "Perry's Chemical Engineers' Handbook", Sixth Edition, McGraw Hill Inc., 1984, Section 18.

20 These devices may be made from or covered with any type of material, such as for example, carbon steel, non-impregnated graphite, and polymeric materials such as polyester.

These devices are generally made from or covered with materials that are resistant to corrosion, under the conditions of the hydrogen chloride purification  
25 step. These materials may be chosen from enamelled steel, metal alloys, metals, polymers, impregnated graphite, non-impregnated graphite, refractory materials, ceramics, cermets, phenolic resins and epoxy resins.

The metal alloys are often Ni-Mo alloys, such as Hastelloy B2 for example.

30 The metals may be chosen from tantalum, gold, silver, molybdenum and nickel, preferably from tantalum and molybdenum, most particularly preferably the metal is tantalum.

The polymers are often chosen from polyolefins, fluoropolymers and sulphur-containing polymers.

35 The polyolefins are preferably chosen from polypropylene and polyethylene, preferably polypropylene.



The fluoropolymers may be completely or partially fluorinated. A partially fluorinated polymer is polyvinylidene fluoride. The perfluoropolymers are often chosen from polytetrafluoroethylene, poly(perfluoropropylvinyl ether) and copolymers of tetrafluoroethylene and hexafluoropropylene.

5 The impregnated graphite may be chosen from graphite impregnated with phenolic resins or with polytetrafluoroethylene.

The preferred materials are preferably chosen from enamelled steel, tantalum, perfluoropolymers, phenolic resins and impregnated graphite.

According to one particular aspect, the equipment for purifying hydrogen  
10 chloride, in particular hydrogen chloride gas, comprises at least one scrubbing column with countercurrent flow, on the one hand, of the hydrogen chloride to be purified and, on the other hand, of the scrubbing agent defined above, said scrubbing column comprising two sections placed one on top of the other. The purified hydrogen chloride gas escapes at the top of the column. At the base of  
15 the column, a fraction (f) is collected that comprises the scrubbing agent, the impurities (as defined above) extracted from the hydrogen chloride to be purified and the portion of this hydrogen chloride that is dissolved in or mixed with the scrubbing agent.

In the scrubbing column that comprises two sections, the first section is  
20 advantageously supplied with at least part of the fraction (f) defined above, withdrawn at the base of this section and recycled in a loop. This fraction (f) may advantageously be treated, during its recycling, fully or partially, by any means known for this purpose, in order to separate therefrom the scrubbing agent loaded with the impurities that it has extracted from the hydrogen chloride.  
25 These means may be those mentioned above in connection with the treatment of the fraction (f). The fraction (f) is preferably treated, at least partly, in at least one stripping column, in order to extract the impurities therefrom, before being recycled to the top of the first section of the scrubbing column.

In the scrubbing column that comprises two sections, the second section,  
30 surmounting the first, is advantageously supplied with fresh scrubbing agent.

The scrubbing column may be equipped with any known type of packing material that promotes exchanges between the component in the gas state to be purified (hydrogen chloride) and the liquid scrubbing agent. An inorganic packing may advantageously be used, in particular, a packing made of  
35 stoneware, ceramic, graphite or metal carbide, preferably made of stoneware or ceramic. A description of the most commonly used materials appears, for

example, in paragraphs 3.4., 3.5. and 3.6. from pages 8-20 and 8-21 of volume B 3 : Unit Operations II of Ullmann's Encyclopedia of Industrial Chemistry, Fifth Completely Revised Edition, published by VCH, 1988. As examples of stoneware or ceramic packing, mention may be made of Raschig rings, Berl saddles, Intalox saddles, ceramic catalyst supports such as Macro Trap type supports and Denstone type supports. In the scrubbing column that comprises two sections, a packing made up of Raschig rings or Berl saddles has been found to be advantageous, with a very particular preference for Berl saddles, in the first section, considering the often quite high liquid flow rate passing through this section. The second section, which only receives the supplementary scrubbing agent, may advantageously be equipped with bubble trays that ensure very good contact of the liquid and gas phases.

The invention also relates in a second aspect to a process for the hydrochlorination of a polyhydroxylated aliphatic hydrocarbon, of an ester of a polyhydroxylated aliphatic hydrocarbon, or of a mixture of the two, to chlorohydrin, using the hydrogen chloride obtained by the purification process according to the invention.

More specifically, the invention also relates to a process for manufacturing a chlorohydrin via reaction between a polyhydroxylated aliphatic hydrocarbon, an ester of a polyhydroxylated aliphatic hydrocarbon, or a mixture of the two, and a chlorinating agent comprising the hydrogen chloride obtained by the purification process according to the invention.

The expression "polyhydroxylated aliphatic hydrocarbon" relates to a hydrocarbon that contains at least two hydroxyl groups attached to two different saturated carbon atoms. The polyhydroxylated aliphatic hydrocarbon may contain, but is not limited to, 2 to 60 carbon atoms.

Each of the carbons of a polyhydroxylated aliphatic hydrocarbon bearing the functional hydroxyl (OH) group cannot possess more than one OH group, and must be of sp<sup>3</sup> hybridization. The carbon atom bearing the OH group may be primary, secondary or tertiary. The polyhydroxylated aliphatic hydrocarbon used in the present invention must contain at least two carbon atoms of sp<sup>3</sup> hybridization bearing an OH group. The polyhydroxylated aliphatic hydrocarbon includes any hydrocarbon that contains a vicinal diol (1,2-diol) or a vicinal triol (1,2,3-triol) including higher orders of these vicinal or adjacent repeat units. The definition of the polyhydroxylated aliphatic hydrocarbon also includes, for example, one or more 1,3-, 1,4-, 1,5- and 1,6-diol functional groups.

The polyhydroxylated aliphatic hydrocarbon may also be a polymer such as polyvinyl alcohol. Geminal diols, for example, are excluded from this class of polyhydroxylated aliphatic hydrocarbons.

The polyhydroxylated aliphatic hydrocarbons may contain aromatic entities or heteroatoms including, for example, heteroatoms of halogen, sulphur, phosphorus, nitrogen, oxygen, silicon and boron type, and mixtures thereof.

Polyhydroxylated aliphatic hydrocarbons that can be used in the present invention include, for example, 1,2-ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,3-propanediol, 1-chloro-2,3-propanediol (chloropropanediol), 2-chloro-1,3-propanediol (chloropropanediol), 1,4-butanediol, 1,5-pentanediol, cyclohexanediols, 1,2-butanediol, 1,2-cyclohexanedimethanol, 1,2,3-propanetriol (also known as "glycerol" or "glycerine"), and mixtures thereof. Preferably, the polyhydroxylated aliphatic hydrocarbon used in the present invention includes, for example, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, chloropropanediol and 1,2,3-propanetriol, and mixtures of at least two of them. More preferably, the polyhydroxylated aliphatic hydrocarbon used in the present invention includes, for example, 1,2-ethanediol, 1,2-propanediol, chloropropanediol and 1,2,3-propanetriol, and mixtures of at least two of them. 1,2,3-propanetriol or glycerol is the most preferable.

The esters of the polyhydroxylated aliphatic hydrocarbon may be present in the polyhydroxylated aliphatic hydrocarbon and/or be produced in the chlorohydrin manufacturing process and/or be manufactured prior to the chlorohydrin manufacturing process. Examples of esters of the polyhydroxylated aliphatic hydrocarbon include ethylene glycol monoacetate, propanediol monoacetates, glycerol monoacetates, glycerol monostearates, glycerol diacetates and mixtures thereof.

The term "chlorohydrin" is defined above. A chlorohydrin that contains at least two hydroxyl groups is also a polyhydroxylated aliphatic hydrocarbon. Therefore, in the hydrochlorination process according to the invention, the starting material and the product of the reaction may each be chlorohydrins. In this case, the chlorohydrin "product" is more chlorinated than the initial chlorohydrin, that is to say that it has more chlorine atoms and fewer hydroxyl groups than the initial chlorohydrin.

In one very suitable embodiment, the chlorohydrin is dichloropropanol and the hydrogen chloride is purified by being brought into contact with a scrubbing

agent that contains dichloropropanol, often by being brought into contact with a scrubbing agent essentially composed of dichloropropanol and the purified hydrogen chloride is intended to be used in a dichloropropanol manufacturing process in which glycerol is reacted with a chlorinating agent that contains this purified hydrogen chloride.

In another embodiment which is also very suitable, the hydrogen chloride is purified by being brought into contact with a scrubbing agent that contains a purge stream from said dichloropropanol manufacturing process, often by being brought into contact with a scrubbing agent essentially composed of this purge stream.

This purge stream typically comprises, per kg, from 150 to 650 g of monochloropropanediol, from 1 to 70 g of glycerol, from 50 to 350 g of dichloropropanol, at most 100 g of water, from 25 to 130 g of diglycerol dichlorohydrin, from 5 to 25 g of diglycerol monochlorohydrin, and from 20 to 200 g of monochloropropanediol esters. The reaction between the polyhydroxylated aliphatic hydrocarbon and the chlorinating agent containing the purified hydrogen chloride may be carried out under temperature, pressure, duration and residence time conditions as described in Application WO 2005/054167 by SOLVAY SA, from page 8, line 25, to page 10, line 10, the content of which is incorporated here by reference.

In a preferred variant of the second aspect, the invention relates to a process for the hydrochlorination of glycerol, of an ester of glycerol, or of a mixture of the two, to dichloropropanol, using the hydrogen chloride obtained by the purification process according to the invention.

In that variant, the glycerol generally contains nitrogen compounds, usually at least one nitrogen compound, as described in Application WO 2009/077528 in the name of SOLVAY SA, from page 1, line 31, to page 3, line 24, and the content of which is incorporated here by reference. The nitrogen compounds can be organic nitrogen compounds or inorganic nitrogen compounds.

The organic nitrogen compounds can be those present in cell of plant origin. They are often selected from the group consisting of amines, urea, proteins, peptides, amino-acids, nucleic acids, glucosinolates, degradation products thereof like isothiocyanates, thiocyanates, nitriles, oxazolidinethiones, phospholipids containing nitrogen, chlorophylls, pheophytines, sinapine, and any mixture of at least two of them.

Examples of phospholipids containing nitrogen are phosphatidyl cholin, phosphatidyl serin and phosphatidyl ethanolamine.

Examples of amino acids free or which could be part of peptides or proteins composition are alanine, arginine, aspartic acid, cystine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophane, tyrosine, valine and any mixture of at least two of them.

Examples of glucosinolates are sinigrine, gluconapine, glucobrassicinapine, glycorucine, glucoberteroine, glucoraphanin, glucoalyssin, gluconasturtine, progoitrine, napoleiferine, glucobrassicine, neoglucobrassicine, and any mixture of at least two of them.

The inorganic nitrogen compounds are frequently selected from the groups consisting of ammonia, hydrazine, chloramines, ammonium inorganic salts, nitrates, nitrites, cyanates, isocyanates, ammonium isothiocyanates, metallic isothiocyanates, and any mixture of at least two of them.

The total nitrogen content of the glycerol expressed as g of N/kg is generally greater than or equal to 0.001, usually greater than or equal to 0.005, often greater than or equal to 0.01, and more often greater than or equal to 0.5. That content is generally lower than or equal to 5, frequently lower than or equal to 2, and more frequently lower than or equal to 1.

That nitrogen content is obtained by chemiluminescence technique.

In that variant, the glycerol generally contains sulfur compounds. The sulfur compounds can be organic sulfur compounds or inorganic sulfur compounds.

Examples of organic sulfur compounds are amino acids containing sulfur, like methionine, cysteine, and cystine, free or being part of peptides or proteins composition, glucosinolates, degradation products thereof like isothiocyanates and thiocyanates, and any mixture of at least two of them.

Examples of inorganic sulfur compounds are sulfates, hydrogensulfates, sulfites, hydrogensulfites, sulfides, hydrogensulfides containing compounds, and any mixture of at least two of them. The inorganic sulfur compound is often a sulfate containing compound.

The total sulfur content of the glycerol expressed as g of S /kg is usually greater than or equal to 0.0001, often greater than or equal to 0.001, and more often greater than or equal to 0.01. That content is generally lower than or equal

- 20 -

to 15, frequently lower than or equal to 10, more frequently lower than or equal to 5 and still more frequently lower than or equal to 1.

In that variant, the glycerol generally contains phosphorus compounds.

The phosphorus compounds can be organic phosphorus compounds or  
5 inorganic phosphorus compounds.

Examples of organic phosphorus compounds are glycerophospholids, like phosphatidyl choline, phosphatidylethanolamine, phosphatidylserine, phosphatidylinositol, polyphosphoinositides, phosphatidylglycerol, phosphatidic acid, and any mixture of at least two of them.

10 Examples of inorganic phosphorus compounds are phosphate, hydrogenphosphates, phosphite and hydrogenphosphites containing compounds, and mixture thereof. The inorganic sulfur compound is often a phosphate containing compound.

The total phosphorus content of the glycerol expressed as g of P /kg is  
15 generally greater than or equal to 0.00001, more generally greater than or equal to 0.0001, usually greater than or equal to 0.001, often greater than or equal to 0.01, and more often greater than or equal to 0.5. That content is generally lower than or equal to 20, frequently lower than or equal to 15, more frequently lower than or equal to 10, and still more frequently lower than or equal to 5, and  
20 yet more frequently lower than or equal to 1.

In that variant, the glycerol generally contains inorganic chlorine compounds.

Examples of inorganic chlorine compounds are chloride containing compounds.

25 The total inorganic chlorine content of the glycerol expressed as g of chloride /kg is generally greater than or equal to 0.001, is usually greater than or equal to 0.05, often greater than or equal to 0.1, and more often greater than or equal to 0.5. That content is generally lower than or equal to 40, frequently lower than or equal to 20, more frequently lower than or equal to 10, and still  
30 more frequently lower than or equal to 5, and yet more frequently lower than or equal to 1.

In that variant, the glycerol may also comprise monoalcohols, usually at least one monoalcohol, such as the monoalcohols described in Application  
WO 2007/144335 in the name of SOLVAY SA, from page 3, lines 26 to 31, and  
35 the content of which is incorporated here by reference.

Examples of monoalcohols are methanol, ethanol, propanol, allyl alcohol, butanol, pentanol, hexanol, heptanol, octanol, methylpropanol, 3-methylbutane-1-ol, 2-methylbutane-1-ol, pentenol, hexenol, 2-phenylethanol, and any mixture of at least two of them.

5       The monoalcohol content of the glycerol expressed as g of methanol/kg of glycerol is usually greater than or equal to 0.001, often greater than or equal to 0.01, more often greater than or equal to 0.1, yet more often greater than or equal to 0.5, still more often greater than or equal to 1 and in particular greater than or equal to 10. That content is generally lower than or equal to 500,  
10       frequently lower than or equal to 300, more frequently lower than or equal to 200, yet more frequently lower than or equal to 100 and still more frequently lower than or equal to 50. The monoalcohol is often chosen from the group consisting of methanol, ethanol, n-propanol, isopropanol, n-butanol, and any mixture of at least two of them.

15       In that variant, the glycerol generally contains diols, usually at least one diol, as described in Application WO 2009/000773 in the name of SOLVAY SA, from page 1, line 30, to page 3, line 21, and the content of which is incorporated here by reference.

20       Examples of diols are 1,2-ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,3-propanediol, 1,2-butanediol, 2,3-butanediol, 1,4-butanediol and any mixture of at least two of them.

      The diol content of the glycerol expressed as g of diol/kg of glycerol is usually greater than or equal to 0.001, often greater than or equal to 0.01, more often greater than or equal to 0.1 and yet more often greater than or equal to 0.5.  
25       That content is generally lower than or equal to 10, frequently lower than or equal to 5, and more frequently lower than or equal to 1. The diol is frequently selected from the group consisting of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, and any mixture of at least two of them.

30       In that variant, the glycerol generally contains glycerol alkyl ethers, usually at least one glycerol alkyl ether, as described in Application WO 2007/144335 in the name of SOLVAY SA, from page 1, line 33, to page 3, line 25, and the content of which is incorporated here by reference.

      Examples of glycerol alkyl ethers are mono-, di- and triethers of glycerol  
35       the alkyl groups of which are independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl groups.

The glycerol alkyl ether content of the glycerol expressed as g of glycerol alkyl ether /kg of glycerol is usually greater than or equal to 0.001, often greater than or equal to 0.01, more often greater than or equal to 0.1, yet more often greater than or equal to 0.5 and still more often greater than or equal to 1. That content is generally lower than or equal to 15, frequently lower than or equal to 10, and more frequently lower than or equal to 5. The glycerol alkyl ether is often chosen from 3-methoxy-1,2-propanediol, 2-methoxy-1,3-propanediol, 3-monopropylenediol or any mixture of at least two of them.

In that variant, the glycerol may have an alkali metal and/or alkaline earth metal content as described in WO 2006/100315 of SOLVAY SA, the content of which is incorporated herein by reference, and especially the passages from page 7, line 11, to page 9, line 10.

In that variant, the glycerol may contain elements other than alkali metals and alkaline earth metals as described in WO 2006/100319 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 2, line 3 to 8, and from page 6, line 20, to page 9, line 14.

In that variant, the glycerol may also comprise metals, often at least one metal. The metal can be present in the metallic form, as a salt, or as a mixture thereof. The metal is often found in the elements of the groups IA, IIA, IVB, VB, VIB, VIIIB, VIIIIB, IB, IIB, IIA, IVA, VA, VIA of the Periodic Table of the Elements.

The metal of Group IA content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.01, often greater than or equal to 0.1, more often greater than or equal to 1, yet more often greater than or equal to 10, still more often greater than or equal to 100 and in particular greater than or equal to 500. That content expressed as g of metal/kg of glycerol is generally lower than or equal to 50, usually lower than or equal to 30, frequently lower than or equal to 10, and more frequently lower than or equal to 5 and yet more frequently lower than or equal to 1. The metal of Group IA is often found in the group consisting of group consisting of Na, K, and mixture thereof.

The metal of Group IIA content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.001, often greater than or equal to 0.005, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05, still more often greater than or equal to 0.1 and in particular greater than or equal to 1. That content is generally lower than or equal to 200, frequently lower than or equal to 150, and more frequently lower



than or equal to 100, yet more frequently lower than or equal to 50, still more frequently lower than or equal to 10. The metal of Group IIA is often found in the group consisting of group consisting of Ba, Ca, Be, Mg and mixture thereof.

The metal of Group IVB content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.001, often greater than or equal to 0.005, more often greater than or equal to 0.01, and yet more often greater than or equal to 0.05. That content is generally lower than or equal to 10, frequently lower than or equal to 5, and more frequently lower than or equal to 1, and yet more frequently lower than or equal to 0.1. The metal of Group IVB is often Ti.

The metal of Group VB content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.001, often greater than or equal to 0.005, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05. That content is generally lower than or equal to 10, frequently lower than or equal to 5, and more frequently lower than or equal to 1, and yet more frequently lower than or equal to 0.1. The metal of Group VB is often V.

The metal of Group VIB content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05. That content is generally lower than or equal to 10, frequently lower than or equal to 5, and more frequently lower than or equal to 1, and yet more frequently lower than or equal to 0.1. The metal of Group VIB is often Cr.

The metal of Group VIIB content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05. That content is generally lower than or equal to 10, frequently lower than or equal to 5, and more frequently lower than or equal to 1, and yet more frequently lower than or equal to 0.1. The metal of Group VIIB is often Mn.

The metal of Group VIII content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05 and still more often greater than or equal to 0.1. That content is generally lower than or equal to 50, frequently lower than or equal

to 30, more frequently lower than or equal to 20, yet more frequently lower than or equal to 10 and still more frequently lower than or equal to 1. The metal of Group VIII is often found in the group consisting of group consisting of Co, Fe, Ni, and mixture of at least two of them.

5       The metal of Group IB content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05. That content is generally lower than or equal to 10, frequently lower than or equal to 5, and more frequently lower than or equal to 1, and yet  
10      more frequently lower than or equal to 0.1. The metal of Group IB is often Cu.

      The metal of Group IIB content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05. That content is generally lower than or equal to 10,  
15      frequently lower than or equal to 5, and more frequently lower than or equal to 1, and yet more frequently lower than or equal to 0.1. The metal of Group IIB is often found in the group consisting of group consisting of Cd, Hg, Zn, and any mixture of at least two of them.

      The metal of Group IIIA content of the glycerol expressed as mg of  
20      metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05. That content is generally lower than or equal to 10, frequently lower than or equal to 5, and more frequently lower than or equal to 1, and yet more frequently lower than or equal to 0.1. The metal of Group IIIA is  
25      often Al.

      The metal of Group IVA content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05. That content is generally lower than or equal to 10,  
30      frequently lower than or equal to 5, and more frequently lower than or equal to 1, and yet more frequently lower than or equal to 0.1. The metal of Group IVA is often found in the group consisting of group consisting of Pb, Sn, and mixture thereof.

      The metal of Group VA content of the glycerol expressed as mg of  
35      metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater

than or equal to 0.05. That content is generally lower than or equal to 1000, frequently lower than or equal to 500, and more frequently lower than or equal to 100, yet more frequently lower than or equal to 10, still more frequently lower than or equal to 1 and in particular lower than or equal to 0.1. The metal of Group VA is often found in the group consisting of group consisting of As, Sb, P, and any mixture of at least two of them.

The metal of Group IVA content of the glycerol expressed as mg of metal/kg of glycerol is usually greater than or equal to 0.0001, often greater than or equal to 0.001, more often greater than or equal to 0.01, yet more often greater than or equal to 0.05. That content is generally lower than or equal to 20, frequently lower than or equal to 10, more frequently lower than or equal to 1, and yet more frequently lower than or equal to 0.1. The metal of Group VIA is often found in the group consisting of group consisting of S, Se, Te, and any mixture of at least two of them.

In that variant, the glycerol may also comprise carboxylic acids, often at least one carboxylic acid.

The carboxylic is usually selected from the group consisting of acetic acid, propionic acid, butyric acid and any mixture of at least two of them.

The carboxylic acid can be a fatty acid. The fatty acid is generally selected from the group consisting of valeric, caproic, caprylic, caprique, lauric, myristic, palmitic, margaric, stearic, arachidic, behenic, lignoceric, hexacosanoic, octacosanoic, melissic, dotriacontanoic, alpha-linoleic, stearidonic, eicosapentanoic, docosahexenoic, linoleic, gamma-linolenic, dihomogamma-linolenic, arachidonic, myristoleic, palmitoleic, petroselinic, oleic, vaccenic, gondoic, claidic, erucic, nervonic, alpha-linolenic, eicosatrienoic, stearidonic, octadecapentaenoic, eicosatetraenoic, eicosapentaenoic, docosapentaenoic, docosahexanoic, ricinoleic, and any mixture of at least two of them.

The carboxylic acid, preferably fatty acid, content of the glycerol expressed as g of carboxylic acid/kg of glycerol is usually greater than or equal to 0.001, often greater than or equal to 0.01, and more often greater than or equal to 0.1. That content is generally lower than or equal to 5, frequently lower than or equal to 3, more frequently lower than or equal to 2, and yet more frequently lower than or equal to 1. The fatty acid is often selected from the group consisting of palmitic acid, oleic acid, linoleic acid, stearic acid, and any mixture of at least two of them.

The carboxylic acid content of the glycerol expressed as mmol of carboxylic acid functionalities / kg is usually greater than or equal to 0.1, often greater than or equal to 0.2, and more often greater than or equal to 0.5. That content is generally lower than or equal to 50, frequently lower than or equal to 40, more frequently lower than or equal to 30, and still more frequently lower than or equal to 20, yet more frequently lower than or equal to 10 and in particular lower than or equal to 1.

In that variant, the glycerol may also comprise carboxylic acids salts, often at least one carboxylic acid salt. Those salts are usually metal salts of the aforementioned carboxylic acids. The metals salts are often found in the group consisting of Na, K, Ba, Ca, Be, Mg, Ti, V, Cr, Mn, Co, Fe, Ni, Cu, Cd, Hg, Zn, Al, Pb, Sn, As, Sb, and any mixture of at least two of them.

The carboxylic acid salt content of the glycerol expressed as g of carboxylate anion / kg is usually greater than or equal to 0.01, often greater than or equal to 0.05, and more often greater than or equal to 1. That content is generally lower than or equal to 80, frequently lower than or equal to 60, more frequently lower than or equal to 40, and still more frequently lower than or equal to 20, yet more frequently lower than or equal to 10 and in particular lower than or equal to 5. The carboxylic acid salt is often a salt of acetic acid.

The carboxylic acid salt content of the glycerol expressed as mmol of carboxylate anion functionalities / kg is usually greater than or equal to 1, often greater than or equal to 2, and more often greater than or equal to 10. That content is generally lower than or equal to 1000, frequently lower than or equal to 800, more frequently lower than or equal to 600, and still more frequently lower than or equal to 400, yet more frequently lower than or equal to 200 and in particular lower than or equal to 100.

In that variant, the glycerol may also comprise alkyl esters of fatty acids, usually at least one alkyl ester of fatty acids, glycerol esters, generally at least one glycerol ester, and salts, commonly at least one salt, as described in Application WO 2007/144335 in the name of SOLVAY SA, from page 5, lines 12 to 20.

The carboxylic acid ester content of the glycerol expressed as mmol of carboxylic acid ester functionalities / kg is usually greater than or equal to 0.1, often greater than or equal to 0.2, and more often greater than or equal to 0.5. That content is generally lower than or equal to 10, frequently lower than or equal to 5, and more frequently lower than or equal to 1.

The alkyl ester of fatty acid is usually an ester of fatty acid frequently selected from the group of the fatty acids aforementioned and with a monoalcohol, often selected from the group consisting of methanol, ethanol, propanol and any mixture of two of them.

5 The alkyl ester of fatty acid content of the glycerol expressed as g of alkyl ester of fatty acid/kg of glycerol is usually greater than or equal to 0.01, often greater than or equal to 0.05, and more often greater than or equal to 0.1. That content is generally lower than or equal to 10, frequently lower than or equal to 5, more frequently lower than or equal to 2, and yet more frequently lower  
10 than or equal to 1. The alkyl ester of fatty acid is often selected from the group consisting of methyl palmitate, methyl oleate, methyl linoleate, methyl linolenate, methyl stearate, and any mixture of at least two of them.

The glycerol ester is usually mono-, a di- or a triester of glycerol with a carboxylic acid frequently selected from the group of the carboxylic acids  
15 aforementioned, often selected from the group consisting acetic acid, propionic acid, fatty acids aforementioned and any mixture of two of them. The esters of glycerol with fatty acids more often encountered are monopalmitate, monooleate, monolinoleate, monolinolenate, monostearate, and any mixture of at least two of them.

20 The alkyl ester of fatty acid content of the glycerol expressed as g of alkyl ester of fatty acid/kg of glycerol is usually greater than or equal to 0.01, often greater than or equal to 0.05, and more often greater than or equal to 0.1. That content is generally lower than or equal to 10, frequently lower than or equal to 5, more frequently lower than or equal to 2, and yet more frequently lower  
25 than or equal to 1.

In that variant, the glycerol may be obtained starting from fossil raw materials or starting from renewable raw materials, preferably starting from renewable raw materials, as described in WO 2005/054167 of SOLVAY SA, the content of which is incorporated herein by reference, and especially the passages  
30 from page 1, line 26, to page 4, line 2

In that variant, the glycerol may also be obtained starting from fossil raw materials or starting from renewable raw materials, preferably starting from renewable raw materials, as described in WO 2009/000773 of SOLVAY SA, the content of which is incorporated herein by reference, and especially the passages  
35 at page 10, lines 16 to 23, and at page 11, lines 4 to 25.

In that variant, the glycerol contains generally an amount of heavy compounds other than glycerol and whose boiling temperature under a pressure of 1 bar absolute is at least 15°C greater than the boiling temperature of dichloropropanol as described in WO 2006/1000316 of SOLVAY SA the content of which is incorporated herein by reference, especially the passages from page 15, line 32, to page 17, line 33.

In that variant, the glycerol may contain glycerol oligomers as described in PCT/EP2009/053766 of SOLVAY SA the content of which is incorporated herein by reference, especially the passages from page 1, line 25, to page 6, line 19.

The glycerol oligomer is generally selected from the group consisting of diglycerol, cyclic diglycerol, polyglycerols containing more than 2 glycerol units, cyclic polyglycerol *i.e.* polyglycerols containing more than 2 glycerol units and at least one ring, and any mixture of at least two of them.

The diglycerol is often selected from the group consisting of 3-(2,3-dihydroxypropoxy)-propane-1,2-diol, 3-(2-hydroxy-1-hydroxymethylethoxy) propane-1,2-diol et 2-(2-hydroxy-1-hydroxymethylethoxy)propane-1,3-diol, and any mixture of at least two of them.

The cyclic diglycerol is often selected from the group consisting of cis- and trans-2,5-bis-(hydroxymethyl)-1,4-dioxane, cis- and trans-2,6-bis-(hydroxymethyl)-1,4-dioxane, cis- and trans-6-hydroxy-2-hydroxymethyl-1,4-dioxepane, et cis- and trans-3,7-dihydroxy-1,5-dioxocane, and any mixture of at least two of them.

The polyglycerol is often selected from the group consisting of triglycerol, tétraglycerol, pentaglycerol, hexaglycerol, heptaglycerol, octaglycerol, and any mixture of at least two of them.

The glycerol oligomer content of the glycerol expressed as g of glycerol oligomer/kg of glycerol is usually greater than or equal to 0.01, often greater than or equal to 0.05, and more often greater than or equal to 0.1. That content is generally lower than or equal to 10, frequently lower than or equal to 5, more frequently lower than or equal to 2, and yet more frequently lower than or equal to 1. The glycerol oligomer is often selected from the group consisting of diglycerol, cyclic diglycerol, preferably aforementioned, and any mixture of at least two of them.

In that variant, the glycerol may contain aldehydes. The aldehydes are often selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, methylbutanal, glyceraldehyde, acrolein, pentenal, hexenal, 5 hexadienal, heptenal, pyruvaldehyde, benzaldehyde, 2-hydroxy-propionaldehyde, 3-hydroxy-propionaldehyde, and any mixture of at least two of them.

The aldehyde content of the glycerol expressed as g of aldehyde/l of glycerol is usually greater than or equal to 0.01, often greater than or equal 10 to 0.05, and more often greater than or equal to 0.1. That content is generally lower than or equal to 10, frequently lower than or equal to 5, more frequently lower than or equal to 2, and yet more frequently lower than or equal to 1. The aldehydes often encountered is glyceraldehyde.

In that variant, the glycerol may contain ketones. The ketones are often 15 selected from the group consisting of acetone, butanone, pentanone, hexanone, heptanone, octanone, nonanone, decanone, undecanone, 2,3-butanedione, cyclopentanone, methylcyclopentenone, acetophenone, hydroxyacetone, dihydroxyacetone, and mixture thereof.

The ketone content of the glycerol expressed as g of ketone/l of glycerol is 20 usually greater than or equal to 0.01, often greater than or equal to 0.05, and more often greater than or equal to 0.1. That content is generally lower than or equal to 10, frequently lower than or equal to 5, more frequently lower than or equal to 2, and yet more frequently lower than or equal to 1.

In that variant, the glycerol may comprise acetals and ketals of the 25 aforementioned aldehydes and ketones with glycerol, such as for example acetal glycerol ketal, 3-hydroxy-propionaldehyde ketal, and mixtures thereof.

In that variant, the glycerol may comprise carotenoids, such as for example, phytoene, phytofluene, cis-beta-carotene, beta-carotene, alpha-carotenes, cis-alpha-carotene, z-carotene, d-carotene, g-carotene, neurosporene, 30 alpha-zeacarotene, beta-zeacarotene, lycopene, and any mixture of at least two of them.

In that variant, the glycerol may comprise aromatic and heteroaromatic derivatives, such as for example, tocopherols (alpha, beta, gamma and delta), tocotrienol, plastoquinone, ubiquinol, furane, methyl-furanes, 35 dimethylfuranes, propylfuranes, pentylmethylfurane, mono- and di- substituted thiophenes, naphthalene, ethylnaphthalene, dimethylnaphthalene, acenaphthene,

phenanthrene, pyrene, fluoranthrene, benzantracene, chrysene, perylene, methoxybenzene, dimethoxybenzene, phenols, phenolic acids, polyphenols, and any mixture of at least two of them.

In that variant, the glycerol may comprise sugar derivatives such as for example, monogalactosyldiacylglycerols, digalactosylglycerols, sterolglycosides, their hydrolysis products and any mixture of at least two of them.

In that variant, the glycerol may contain water.

The water content of the glycerol expressed as g of water/ kg of glycerol is usually greater than or equal to 0.01, often greater than or equal to 0.05, and more often greater than or equal to 0.1. That content is generally lower than or equal to 200, frequently lower than or equal to 100, more frequently lower than or equal to 50, yet more frequently lower than or equal to 10, still more frequently lower than or equal to 5 and in particular lower than or equal to 1.

In that variant, the glycerol may exhibit an ash content expressed in weight per cent, generally higher than of 0.01, often greater than or equal to 0.05, and more often greater than or equal to 0.1. That content is generally lower than or equal to 40, frequently lower than or equal to 20, more frequently lower than or equal to 10, yet more frequently lower than or equal to 5, and in particular lower than or equal to 1.

In that variant, the glycerol may exhibit a MONG (non glycerinous organic matter) content expressed in weight per cent, generally higher than of 0.01, often greater than or equal to 0.05, and more often greater than or equal to 0.1. That content is generally lower than or equal to 80, frequently lower than or equal to 60, more frequently lower than or equal to 30, yet more frequently lower than or equal to 20, and in particular lower than or equal to 10.

In that variant, the glycerol may contain other compounds such n-alkanes linear, of formula  $\text{CH}_3(\text{CH}_2)_x\text{CH}_3$ , with an odd or even number of carbon atoms from 11 to 35, branched alkanes with an odd or even number of carbon atoms from 11 to 35, alkyl esters of formula  $(\text{CH}_3(\text{CH}_2)_x\text{COO}(\text{CH}_2)_y\text{CH}_3$ , with an even number of carbon atoms from 34 to 62, fatty alcohols (primary) of formula  $\text{CH}_3(\text{CH}_2)_y\text{CH}_2\text{OH}$  with an even number of carbon atoms from 22 to 32, fatty aldehydes of formula  $\text{CH}_3(\text{CH}_2)_y\text{CHO}$  with an even number of carbon atoms from 22 to 32, ketones of formula  $\text{CH}_3(\text{CH}_2)_x\text{CO}(\text{CH}_2)_y\text{CH}_3$  with an odd number of carbon atoms from 23 to 33, fatty alcohols (secondary) of formula  $\text{CH}_3(\text{CH}_2)_x\text{CHOH}(\text{CH}_2)_y\text{CH}_3$  with an odd number of carbon atoms from 23 to 33,  $\beta$ -diketones of formula  $\text{CH}_3(\text{CH}_2)_x\text{COCH}_2\text{CO}(\text{CH}_2)_y\text{CH}_3$  with an



odd number of carbon atoms from 27 to 33, triterpenols, sterols like cholesterol, campesterol, stigmasterol and sitosterol,  $\alpha$ -amyrin,  $\beta$ -amyrin, uvaol, lupeol, erythriol, triterpenoid acids like ursolic acid, oleanolic acid, *etc.*, hydroxy- $\beta$ -diketones, oxo- $\beta$ -diketones, alkenes (squalene), branched carboxylic acids, 5 branched esters, acetates and benzoates of aliphatic alcohols, methyl, phenylethyl and triterpenoid esters, ceramides, and any mixture of at least two of them.

In that variant, the reaction between glycerol and the chlorinating agent the hydrogen chloride may be carried out in a reaction medium such described in WO 2006/106154 of SOLVAY SA, the content of which is incorporated herein 10 by reference, especially the passages from page 14, line 15, to page 17, line 10.

In that variant, the reaction with the chlorinating agent may be carried out in the presence of a catalyst, preferably a carboxylic acid or a carboxylic acid derivative, as described in Patent Application WO 2005/054167, from page 6, line 24, to page 7, line 35 in the name of SOLVAY SA, the content of which is 15 incorporated herein by reference.

In that variant, the reaction with the chlorinating agent may be carried out for a catalyst concentration, at a temperature, at a pressure and at a residence time such described in WO 2005/054167 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 8, line 1, 20 to page 10, line 10.

In that variant, the reaction with the chlorinating agent may be carried out such described in WO 2007/054505 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 1, line 24 to page 6, line 18.

In that variant, the process for manufacturing dichloropropanol may be carried in equipments made of or coated with materials which are resistant to the corrosion by the chlorinating agent under the process conditions, such as described in WO 2005/054167 of SOLVAY SA, the content of which is 25 incorporated herein by reference, especially the passages from page 6, lines 3 to 23.

In that variant, the process for manufacturing dichloropropanol may be carried in equipments made of or coated with materials which are resistant to the corrosion by the chlorinating agent under the process conditions, such as described in WO 2006/100317 of SOLVAY SA, the content of which is 35 incorporated herein by reference, especially the passages from page 23, line 22, to page 27, line 25.

In that variant, the process for manufacturing dichloropropanol according to the invention may be carried in equipments made of or coated with materials which are resistant to the corrosion by the chlorinating agent under the process conditions, such as described in WO 2009/043796 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from  
5 page 1, line 30, to page 9, line 17, and from page 19, line 25, to page 20, line 33.

In that variant, the reaction with the chlorinating agent may be carried out under stirring with a stirring system such described in WO 2008/145729 of SOLVAY SA, the content of which is incorporated herein by reference,  
10 especially the passages from page 1, line 30, to page 2, line 33, and from page 6, line 22, to page 14, line 31.

In that variant, the reaction with the chlorinating agent may be carried out in a liquid reaction medium such described in WO 2006/106154 of SOLVAY SA, the content of which is incorporated herein by reference,  
15 especially the passages from page 1, line 29, to page 2, line 6, and from page 14, line 15, to page 17, line 10.

In that variant, the reaction with the chlorinating agent may be carried out in a reactor the feeding of which is described in WO 2008/107468 of SOLVAY SA, the content of which is incorporated herein by reference,  
20 especially the passages from page 1, line 29, to page 4, line 27, and from page 5, line 34, to page 9, line 17.

In that variant, a separation of the dichloropropanol from the other compounds of the reaction mixture may be carried out such described in WO 2005/054167 of SOLVAY SA, the content of which is incorporated herein  
25 by reference, especially the passages from page 12, line 1, to page 17, line 20.

In that variant, a separation of the dichloropropanol from the other compounds of the reaction mixture may be carried out according to methods such described in WO 2006/100313 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages at page 2, lines 1 to 23,  
30 and from page 21, line 7, to page 25, line 25.

In that variant, a separation of the dichloropropanol from the other compounds of the reaction mixture may be carried out according to methods such described in WO 2006/100314 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages at page 2, lines 6 to  
35 page 3, line 4, and from page 18, line 33, to page 22, line 29.

In that variant, a separation of the dichloropropanol from the other compounds of the reaction mixture may be carried out according to methods such described in WO 2006/100320 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 1, line 30, to  
5 page 2, line 23, and from page 6, line 25, to page 10, line 28.

In that variant, a separation of the dichloropropanol from the other compounds of the reaction mixture may be carried out according to methods such described in WO 2006/100315 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages at page 2, lines 3 to 29,  
10 and from page 23, line 3, to page 24, line 13.

In that variant, a separation of the dichloropropanol from the other compounds of the reaction mixture may be carried out according to methods such described in WO 2008/110588 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 1, line 31, to  
15 page 27, line 25.

In that variant, the dichloropropanol is generally obtained as a mixture of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol isomers such described in WO 2006/100319 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages from page 23, line 34, to page 24, line 29.

In that variant, the dichloropropanol may contain halogenated ketones such described in WO 2006/100311 of SOLVAY SA, the content of which is incorporated herein by reference, especially the passages at page 2, lines 22  
20 to 34, and from page 22, line 8, to page 23, line 35.

The invention also relates in a third aspect to a process for manufacturing an epoxide, comprising the process for manufacturing the chlorohydrin, in which the chlorohydrin obtained via reaction between the polyhydroxylated aliphatic hydrocarbon, the ester of the polyhydroxylated aliphatic hydrocarbon or the mixture of the two, and the chlorinating agent containing the purified hydrogen chloride, is subjected to a dehydrochlorination reaction, often in the presence of a  
25 basic agent.

The chlorohydrin may be chosen from chloroethanol, chloropropanol, chloropropanediol, dichloropropanol and mixtures of at least two of them. The chlorohydrin is often dichloropropanol.

The epoxide may be chosen from ethylene oxide, propylene oxide, glycidol, epichlorohydrin, or mixtures of at least two of them. The epoxide is  
35 often epichlorohydrin.

The basic agent may be chosen from alkali or alkaline-earth metal oxides, hydroxides, carbonates, hydrogen carbonates, phosphates, hydrogen phosphates and borates, and mixtures thereof. Alkali and alkaline-earth metal oxides and hydroxides are preferred.

5 In one particular embodiment the chlorohydrin is dichloropropanol, the basic agent is an alkali and/or alkaline-earth metal hydroxide and the epoxide is epichlorohydrin.

In the process for manufacturing the epoxide according to the invention, the dehydrochlorination reaction may be carried out such as described in  
10 WO 2005/054167 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passage from page 19, line 12 to page 22, line 30.

In the process for manufacturing the epoxide according to the invention, the dehydrochlorination reaction may be carried out such as described in  
15 WO 2006/100311 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passages at page 2, lines 22 to 25, and from page 22, line 28 to page 23, line 35.

In the process for manufacturing the epoxide according to the invention, the dehydrochlorination reaction may be carried out such as described in  
20 WO 2008/101866 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passage from page 2, line 1 to page 13, line 16.

In the process for manufacturing the epoxide according to the invention, the dehydrochlorination reaction may be carried out such as described in  
25 WO 2008/152045 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passages from page 9, line 22, to page 13, line 31.

In the process for manufacturing the epoxide according to the invention, the dehydrochlorination reaction may be carried out such as described in  
30 WO 2008/152043 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passages from page 7, line 35, to page 8, line 25.

The process for manufacturing the epoxide according to the invention may be integrated in a global scheme for preparing dichloropropanol such as  
35 described in WO 2006/106155 in the name of SOLVAY SA, the content of

which is hereby incorporated by reference, more specifically the passages at page 2, lines 26 to 31, and from page 22, line 10 to page 23, line 19.

In the process for manufacturing the epoxide according to the invention, the dehydrochlorination reaction may be carried out such as described in  
5 WO 2006/100318 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passages at page 2, lines 23 to page 3, line 26, and from page 24, line 17 to page 31, line 18.

The process for manufacturing the epoxide according to the invention may also comprise a step of treating water effluents such as described in  
10 WO 2009/095429 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passages from page 1, line 24, to page 27, line 26.

The invention also relates to a process for manufacturing an epoxy derivative selected from the group consisting of epoxy resins, glycidyl ethers, glycidyl esters, glycidyl amides, glycidyl imides, glycidyl amines, products that can be used as coagulants, wet-strength resins, cationization agents, flame retardants, ingredients for detergents, epichlorohydrin elastomers, halogenated polyethers-polyols, monochloropropanediol, and any mixture of at least two of them, comprising the process for manufacturing the epoxide in which the  
20 epoxide is epichlorohydrin, and in which the epichlorohydrin is subjected to a reaction with at least one compound chosen from monoalcohols, monocarboxylic acids, polyols, polyamines, amino alcohols, polyimides, polyamides, polycarboxylic acids, ammonia, amines, polyaminoamides, polyimines, amine salts, phosphoric acid, phosphoric acid salts, phosphorus oxychlorides, 25 phosphoric acid esters, phosphonic acids, esters of phosphonic acids, salts of phosphonic acids, phosphinic acids, esters of phosphinic acids, salts of phosphinic acids, phosphine oxides, phosphines, ethoxylated alcohols, alkylene or phenylene oxides, and mixtures of at least two of them, or in which the epichlorohydrin according to the invention is subjected to a homopolymerization reaction, or in which epichlorohydrin is subjected to a reaction of  
30 oligomerisation, of co-oligomerisation, of condensation, of dehydrochlorination and of hydrolysis, with water, or with a di- or polyhydroxylated compound which may optionally be halogenated and/or have ether oxide bonds and/or double bonds capable of being halogenated in a subsequent stage, or wherein  
35 epichlorohydrin is subjected to a reaction with water.

The process for manufacturing the epoxy derivative according to the invention, may be carried out, such as described in Application WO 2008/152045 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passages from page 32, line 6, to page 63, line 4, and in Application WO 2008/152044 in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passages from page 13, line 22, to page 44, line 8 and in Application PCT/EP2009/053766, in the name of SOLVAY SA, the content of which is hereby incorporated by reference, more specifically the passages from page 27, line 10, to page 33, line 7.

The purification process and the equipment according to the invention will now be illustrated with reference to Figure 1. This figure schematically represents a practical embodiment of aspects of the invention. The hydrogen chloride gas originates from an isocyanate manufacturing unit and is contaminated with impurities essentially composed of monochlorobenzene in an amount of 250 ppm.

According to a first embodiment, the scrubbing agent is essentially composed of dichloropropanol that originates from a plant for manufacturing dichloropropanol by hydrochlorination of glycerol using hydrogen chloride. The purified hydrogen chloride is conveyed to a glycerol hydrochlorination unit.

A first gas stream containing the hydrogen chloride to be purified is introduced via the line (4) into section (2) of the scrubbing column (1). A first liquid stream essentially composed of fresh dichloropropanol (necessary for boosting the supply, considering the entrainment by vapour pressure of the dichloropropanol to the glycerol hydrochlorination unit via the purified hydrogen chloride and the removal of dichloropropanol via the purge system (see below)) is introduced via the line (5) into section (3) of the scrubbing column (1). Section (2) of the scrubbing column (1) is preferably packed with Berl saddles. Section (3) of the scrubbing column (1) is preferably packed with bubble trays. A second liquid stream comprising the dichloropropanol, in which the impurities extracted from the hydrogen chloride to be purified are dissolved, and a portion of this hydrogen chloride is withdrawn at the bottom of the column (1) via the line (6) and recycled in a loop to the top of section (2) via the pump (7) and the line (8). A portion of this second liquid stream, which constitutes a third liquid stream, is drawn off via the line (9) and supplies a stripping column (10). A second gas stream comprising most of the hydrogen chloride dissolved in the

third liquid stream is drawn off from the stripping column (10) and sent back to section (2) of the scrubbing column (1) via the line (12). A fourth liquid stream comprising the dichloropropanol enriched with impurities from the hydrogen chloride is drawn off from the column (10) and sent to a distillation column (16) via the line (11). A fifth liquid stream enriched with impurities from the hydrogen chloride, the boiling point of which is below that of dichloropropanol, is drawn off from the column (16) via the line (14). This fifth stream may be sent to a storage unit or to a high-temperature oxidation unit. A sixth liquid stream enriched with dichloropropanol is drawn off from column (16) and sent to section (2) of the scrubbing column (1) via the line (17). A seventh liquid stream enriched with impurities from the hydrogen chloride, the boiling point of which is above that of dichloropropanol, is drawn off from the column (16) via the line (15). This seventh stream may be sent to a storage unit or to a high-temperature oxidation unit.

A third gas stream comprising the purified hydrogen chloride gas exits the column (1) via the line (13) in order to be conveyed to the glycerol hydrochlorination unit.

By virtue of this equipment, the monochlorobenzene content of the HCl may be reduced from 250 ppm to less than 10 ppm in the third gas stream exiting the column (1) via the line (13). This operation therefore makes it possible to effectively purify the hydrogen chloride of monochlorobenzene. In this way a product is obtained that can be used, without drawbacks, for a glycerol hydrochlorination step.

According to a second embodiment, the scrubbing agent is essentially composed of a purge stream that originates from a plant for manufacturing dichloropropanol by hydrochlorination of glycerol using hydrogen chloride. The purified hydrogen chloride is conveyed to a glycerol hydrochlorination unit.

In a first variant of the second embodiment, the procedure of the first embodiment is followed, except that the purge stream is used instead of the dichloropropanol in the various lines and columns.

In a second variant of the second embodiment, the procedure of the first variant is followed, except that line (17) does not exist.

In a third variant of the second embodiment, the procedure of the first variant is followed, except that the distillation column (16) and the lines (14), (15) and (17) do not exist, and the stream drawn off via the line (11) supplies a high-temperature oxidation unit.

In a fourth variant of the second embodiment, the procedure of the second variant is followed, except that the stripping column (10) and the lines (11) and (12) do not exist, and the stream drawn off via the line (9) supplies a high-temperature oxidation unit.

5 Example 1 (according to the invention)

Hydrogen chloride has been introduced at a constant flow rate through a gas dispersion tube made of fritted glass in liquid 1,3-dichloropropan-2-ol contained in a glass flask maintained at 25°C, and at a pressure of 1 bar. The hydrogen chloride contained initially chlorobenzene at a concentration of  
10 1000 ppm by weight. The flow rate of the hydrogen chloride has been set in order to treat 1.6 g of gas with 1 g of 1,3-dichloropropan-2-ol in 2 h. The residence time was about 5 s. The hydrogen chloride at the output of the treatment has been sampled and analyzed several times during the treatment and at the end of the treatment. The content in chlorobenzene of the gas was always  
15 lower than 300 ppm by weight.

Example 2 (according to the invention)

The conditions of example 1 have been used except that the flow rate of the hydrogen chloride has been set in order to treat 2.6 g of gas with 1 g of 1,3-dichloropropan-2-ol in 2 h. The residence time was about 2.5 s. The  
20 hydrogen chloride at the output of the treatment has been sampled and analyzed several times during the treatment and at the end of the treatment. The content in chlorobenzene of the gas was always lower than 300 ppm by weight.

Example 3 (according to the invention)

The conditions of example 1 have been used except that the flow rate of  
25 the hydrogen chloride has been set in order to treat 6.5 g of gas with 1 g of 1,3-dichloropropan-2-ol in 4 h. The residence time was about 2.5 s. The hydrogen chloride at the output of the treatment has been sampled and analyzed several times during the treatment and at the end of the treatment. The content in chlorobenzene of the gas was always lower than 500 ppm by weight.



CLAIMS

- 1 – Process for purifying hydrogen chloride, comprising at least one step of bringing said hydrogen chloride into contact with a scrubbing agent containing at least one chlorohydrin.
- 5        2 – Process according to Claim 1, in which at least one portion of the hydrogen chloride is in the gaseous state.
- 3 – Process according to Claim 1 or 2, in which the hydrogen chloride contains aromatic organic compounds.
- 4 – Process according to any one of Claims 1 to 3, in which the hydrogen  
10 chloride is the by-product of the manufacture of organic isocyanates.
- 5 – Process according to Claim 4, in which the hydrogen chloride is the by-product of the manufacture of organic isocyanates by reacting phosgene with an organic amine.
- 6 – Process according to any one of Claims 3 to 5, in which the aromatic  
15 organic compounds are chloroaromatic compounds.
- 7 – Process according to any one of Claims 1 to 6, in which the chlorohydrin is chosen from monochloropropanediol, dichloropropanol, and mixtures thereof.
- 8 – Process according to any one of Claims 1 to 7, in which the scrubbing  
20 agent additionally contains at least one compound chosen from water, alcohols, aldehydes, ketones, carboxylic acids, carboxylic acid esters, ethers, halogenated hydrocarbons, epoxides, metals, and mixtures of at least two of them.
- 9 – Process according to any one of Claims 1 to 8, in which the scrubbing agent is substantially composed of dichloropropanol in the liquid state.
- 25        10 – Process according to any one of Claims 1 to 9, in which the step of bringing into contact with the scrubbing agent is carried out at a temperature between 10 and 120°C, and at a pressure between 1 and 20 bar absolute.

11 – Process according to any one of Claims 1 to 10, in which the flow of the scrubbing agent is between 0.5 and 50 % by weight relative to the flow of hydrogen chloride to be purified.

- 5 12 – Process according to any one of Claims 1 to 11, in which the hydrogen chloride is intended to be used in a reaction for the hydrochlorination of a polyhydroxylated aliphatic hydrocarbon.

- 10 13 – Process for manufacturing a chlorohydrin, in which the process according to any one of Claims 1 to 12 is carried out in order to obtain purified hydrogen chloride, and in which a polyhydroxylated aliphatic hydrocarbon, an ester of a polyhydroxylated aliphatic hydrocarbon or a mixture of the two is reacted with a chlorinating agent containing said purified hydrogen chloride in order to obtain the chlorohydrin.

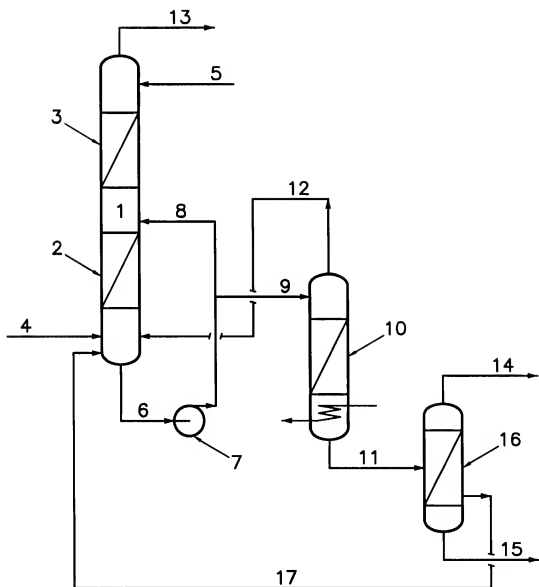
- 15 14 – Process for manufacturing an epoxide, in which the process according to Claim 13 is carried out in order to obtain a chlorohydrin and in which said chlorohydrin is subjected to a dehydrochlorination reaction.

- 16 15 – Process for manufacturing an epoxy derivative selected from the group consisting of epoxy resins, glycidyl ethers, glycidyl esters, glycidyl amides, glycidyl imides, glycidyl amines, products that can be used as coagulants, wet-strength resins, cationization agents, flame retardants, ingredients for detergents, epichlorohydrin elastomers, halogenated polyethers-  
20 polyols, monochloropropanediol, and any mixture of at least two of them, comprising the process according to Claim 14, in which the epoxide is epichlorohydrin and in which the epichlorohydrin is subjected to a reaction with at least one compound chosen from monoalcohols, monocarboxylic acids,  
25 polyols, polyamines, amino alcohols, polyimides, polyamides, polycarboxylic acids, ammonia, amines, polyaminoamides, polyimines, amine salts, phosphoric acid, phosphoric acid salts, phosphorus oxychlorides, phosphoric acid esters, phosphonic acids, esters of phosphonic acids, salts of phosphonic acids, phosphinic acids, esters of phosphinic acids, salts of phosphinic acids, phosphine  
30 oxides, phosphines, ethoxylated alcohols, alkylene or phenylene oxides, and mixtures of at least two of them, or in which the epichlorohydrin according to the invention is subjected to a homopolymerization reaction, or in which epichlorohydrin is subjected to a reaction of oligomerisation, of co-oligomerisation, of condensation, of dehydrochlorination and of hydrolysis, with

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water, or with a di- or polyhydroxylated compound which may optionally be halogenated and/or have ether oxide bonds and/or double bonds capable of being halogenated in a subsequent stage, or wherein epichlorohydrin is subjected to a reaction with water.

Fig. 1



**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C01B7/07 C07D301/02 C07D303/08 C08G59/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	FR 2 881 732 A (SOLVAY [BE]) 11 August 2006 (2006-08-11) cited in the application abstract claims 1-8	1-15
A	----- MYSZKOWSKI J ET AL: "Removal of chlorinated organic impurities from hydrogen chloride" CA HOST- CA, 8 December 1990 (1990-12-08), XP002352444 abstract ----- -/-	1-15

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 November 2009

Date of mailing of the international search report

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## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p>MILCHERT E ET AL: "Recovering hydrogen chloride and organic chloro compounds from the reaction mixture in the chlorination of ethylene"            CA HOST- CA, 15 August 1995 (1995-08-15),            XP002352443            abstract</p> <p>-----</p>	1-15
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